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Improved Temperature Stability of Sulfur Dioxide Samples Collected by the Federal Reference Method

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IMPROVED TEMPERATURE STABILITY OF SULFUR DIOXIDE SAMPLES COLLECTED BY THE FEDERAL REFERENCE METHOD

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The parameters initially evaluated were pH, tetrachloromercurate (TCM), and chloride ion concentration. With the development of a modified collecting solution based on these studies (0.04M TCM with a $[Hg^{++}]$ to $[Cl^-]$ of 1/16), collection efficiency and order of reaction of the modified collecting reagent were determined.

Using an Arrhenius plot of the experimental data, an equation was derived which describes the relationship between rate of decay of collected SO_2 samples and temperature. The modified collecting reagent was found to increase the stability of the collected SO_2 samples over a wider temperature range. Thus the effect of temperature was reduced by about 10°C when compared against previous SO_2 FRM data. The improvements developed here could be used to liberalize the present temperature specification required to insure the stability of collected SO_2 samples.

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SECTION 1

INTRODUCTION

Previous research (1-9) has indicated that samples collected by the Federal Reference Method (FRM) for Determination of Sulfur Dioxide Concentration in the Ambient Air(10) have temperature dependent stability problems both during and after sampling. To minimize this instability problem several suggestions have been proposed:

(a) relocation of the present sampling site to a temperature controlled structure,

(b) redesign of the sampler and shipping container to maintain certain sample temperature specifications both during and prior to the time of analysis (i.e., thermoelectric coolers, temperature controlled shipping containers),(11)

(c) the use of continuous monitors; and

(d) stabilization of the formed dichlorosulfitomercurate complex by adjusting the reagent concentrations and conditions.

In an attempt to minimize the cost suggested by (a), (b), and (c), an investigation was begun to reduce the temperature dependent decay of the formed complex to its minimum while keeping the reagents the same. To evaluate the other alternatives would require an extended time period for a full scale research project which would not meet our intended purpose of a short time solution. The results of these experiments to adjust reagent concentration are discussed in this report.

SECTION 2

EXPERIMENTAL

The specific reagents and procedures used for sample preparation and analysis are those specified in the Federal Register for the determination of SO_2 concentration in the atmosphere (Pararosaniline Method) (10). Other pertinent experimental details not contained in that procedure are described in the following sections:

SAMPLE PREPARATION

Unless otherwise described, all samples containing sulfur dioxide (SO_2) were prepared using the indicated tetrachlormercurate (TCM) and sodium metabisulfite concentrations.

During the collection efficiency studies, two different SO_2 permeation tubes (National Bureau of Standards, Standard Reference Material #1627, 2 cm in length) were used to generate the test atmospheres using typical generation apparatus (10).

SAMPLE ABSORBING REAGENT PREPARATION

All TCM concentrations were prepared as described in the report with the nominal TCM concentration being 0.04 M with a $[Hg^{++}]/[Cl^{-}]$ ratio of 1/4.

SAMPLE TEMPERATURE CONTROL

The indicated temperatures of the experimental samples were maintained by placing each sample in a constant temperature bath with the temperature

of each maintained to ± 0.1°C. This was accomplished by submerging the capped sample below the solution volume line.

SAMPLE ANALYSIS

At selected times, portions of the thermostated samples were taken and rapidly cooled to 22.0°C in a constant temperature bath to prevent further decay before analysis. An aliquot (10 ml) of each of these portions was taken and analyzed immediately for SO_2 concentration by the SO_2 Federal Reference Method (FRM). A larger sample aliquot than that specified in the FRM (5 ml) was taken because previous experiments conducted in our laboratory indicated that much better precision and accuracy were obtained at lower SO_2 concentrations by increasing the aliquot size. The temperature at which the color was developed in the analytical procedure was also 22.0°C.

DATA ANALYSIS

Best fit regression analysis equations were calculated using a programmable calculator-plotter.

SECTION 3

RESULTS AND DISCUSSION

When ambient SO_2 dissolves in an aqueous solution containing mercuric chloride, potassium chloride, and ethylenediaminetetraacetate disodium salt (EDTA) of specified proportions, several equilibriums (12-13) are established, the major ones being shown in Figure 1. The equations show that sulfur dioxide is present in three different forms before a complex is formed:

(a) sulfurous acid;

(b) bisulfite ion;

(c) sulfite ion.

At a pH of approximately 4, which is the pH of the SO_2 FRM absorbing reagent, the major species found is the bisulfite ion. This is the species that complexes with the tetrachloromercurate to form the dichlorosulfitomercurate complex. Although a small concentration of $SO_3^=$ is in equilibrium, oxidation of this species is thought to be the cause of loss of SO_2, since the formation of $SO_4^=$ is not reversible. This causes a constant equilibrium condition to be established at the expense of the bisulfite ion and continuously depletes the concentration of bisulfite available to be complexed by the tetrachloromercurate. Another problem with the TCM is its ionization in dilute solutions(5) which reduces pH and lowers collection efficiency.

Possible solutions to these problems are:

(a) reducing the amount of $SO_3^=$ formed by controlling pH and making

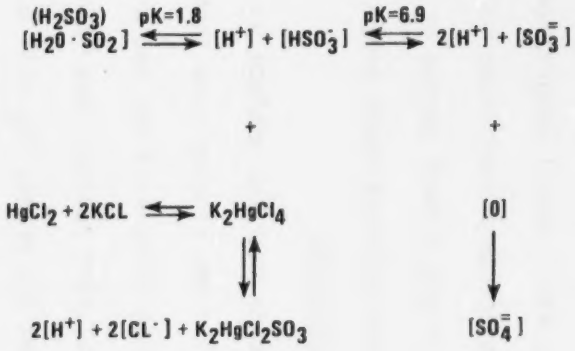

Figure 1. SO_2 in TCM equilibrium equations.

the HSO_3^- the most favorable species;

(b) increase the amount of TCM available as a complexing agent by decreasing the ionization of the TCM by:

1. increasing the TCM concentration, and
2. increasing the Cl^- ion concentration.

The other reagents used in the analytical procedure of the SO_2 FRM could be examined for the effect on decay, but drastic changes in reagent makeup, even if successful, would entail lengthy evaluations and equivalance studies which would preclude a short time solution. If a need does exist to significantly alter the current method or to develop a new method, research oriented groups must continue these projects.

EFFECT OF pH AND TCM CONCENTRATION

Previous studies indicate that the optimum pH of the SO_2 FRM absorbing reagent is 4.0 ± 1. (5)(15) The studies show that optimum color can be developed and that collection efficiency was not adversly affected in this range. As the pH of the solution becomes less than 2, the SO_2 becomes less soluble in the solution, and the excess SO_2 will be flushed out by the air bubbling through the sampling system. Above a pH of 7 the equilibrium will favor more $SO_3^=$ formation, which could result in eventual loss as sulfate.

To examine the effect of pH, solutions were prepared at pH = 3 and pH = 5. Four concentrations of TCM (0.01, 0.04, 0.1, and 0.25 M) were examined at each pH. The pH was adjusted with HCl or NaOH dropwise and the pH measured with a calibrated pH meter.

A simulated SO_2 sample concentration of 165 µg SO_2/m^3 (using a sulfite standard solution containing 0.95 µg SO_2/ml and an assumed sampling rate of 200 cc/min for 24 hours using 50 ml of absorbing reagent) was used as the sample.

This concentration was chosen because it is approximately twice the primary SO_2 arithmetic mean standard and about one half the maximum 24 hour concentration(10).

Before subjecting these samples, with their specific absorbing reagents, to a temperature study, basic information such as wavelength maximum and color development time for the solutions had to be determined. These data are shown in Table 1.

Since these samples showed full color development in 30 minutes this was the time selected for these samples.

Figures 2 and 3 for pH 3 and 5, respectively, show the effect of 50°C on the same concentration (165 µg SO_2/m^3) prepared in 0.01, 0.04, 0.1, and 0.25 M TCM. The curves indicate that as the TCM concentration increases, the rate of decay of the SO_2 concentration decreases, and as the TCM concentration increases the y-intercept, which indicates sensitivity, decreases. (No further study to describe the actual sensitivity of the method or any of its modifications was continued). Table 2 summarizes the effect of pH 3 and 5. No significant difference in decay rate was found between the results of pH 3 and 5. Although at 0.25 M TCM pH = 3, the decay rate reached a minimum of 41 percent per day, a substantial increase in TCM concentration was necessary with the associated problem of disposal of larger quantities of mercury when the reagent is spent.

EFFECT OF INCREASE OF CHLORIDE ION

It was originally reported (14) that the most stable dichlorosulfitomercurate complex was formed when the ratio of [NaCl] to [$HgCl_2$] was equal to 2. This gave a [Hg^{++}] to [Cl^-] ion concentration of 1 to 4. This was also found to be the case when Scaringelli modified(15) the West-Gaeke pro-

TABLE 1. EFFECT OF pH and TCM CONCENTRATION ON WAVELENGTH MAXIMUM AND TIME OF FULL COLOR DEVELOPMENT

	Concentration	λ Max	Time of Max Color
pH 3	0.01 M TCM	548 nm	15-45 min
	0.04 M TCM	548 nm	15-60 min
	0.1 M TCM	548 nm	15-60 min
	0.25 M TCM	555 nm	15-60 min
pH 5	0.01 M TCM	548 nm	30-60 min
	0.04 M TCM	548 nm	15-60 min
	0.1 M TCM	548 nm	15-60 min
	0.25 M TCM	555 nm	15-60 min

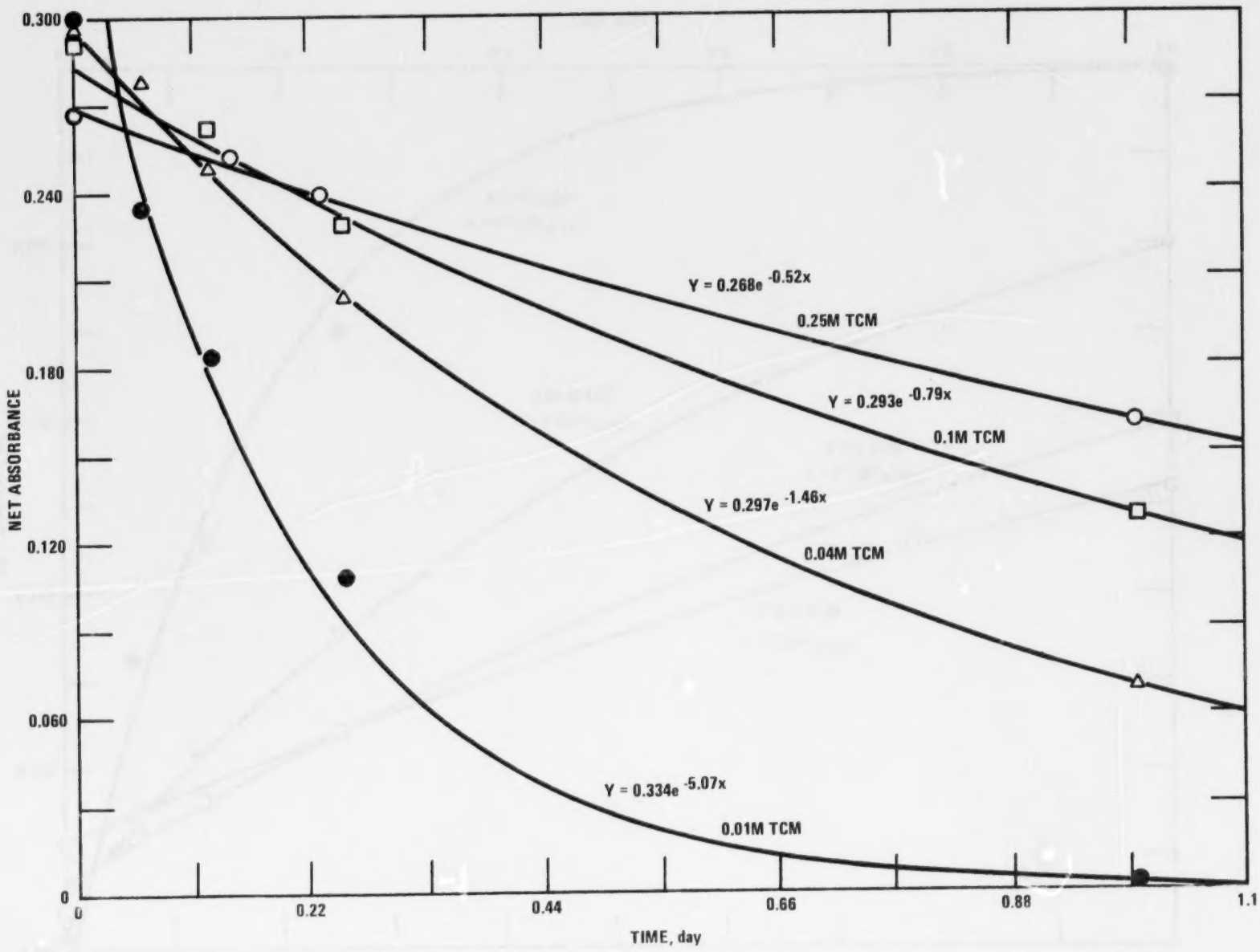

Figure 2. Effect of pH and TCM concentration of stability of the dichlorosulfitomercurate complex, pH = 3, 50°C.

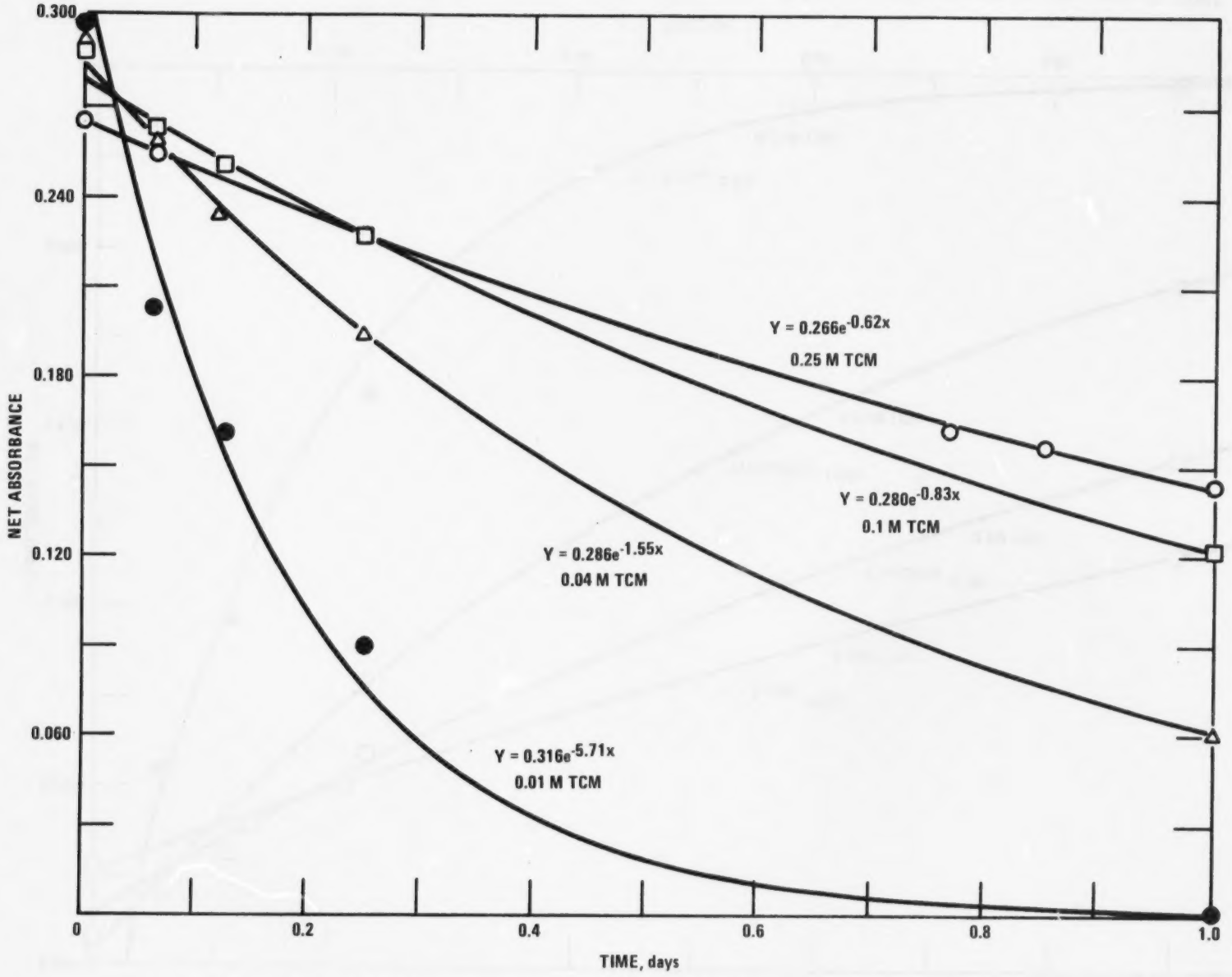

Figure 3. Effect of pH and TCM concentration on stability of the dichlorosulfitomercurate complex, pH=5, 50°C.

TABLE 2. SUMMARY OF THE EFFECTS OF pH AND TCM CONCENTRATION ON STABILITY OF THE DICHLOROSULFITOMERCURATE COMPLEX, 50°C

$(Y = Ae^{BX})$

	pH ≅ 3			pH ≅ 5		
TCM CONC.	A	B	Percent Decay / Day	A	B	Percent Decay / Day
0.01 M	0.334	-5.07	99+	0.316	-5.71	99+
0.04 M	0.297	-1.46	77	0.286	-1.55	79
0.1 M	0.283	-0.79	55	0.280	-0.83	56
0.25 M	0.268	-0.52	41	0.266	-0.62	46

X = Time, Days

Y = Sample Absorbance

cedure, which is the procedure used as the SO_2 FRM. To reexamine the temperature stability of the formed complex at various ratios of $[Hg^{++}]$ to $[Cl^-]$, standard solutions were prepared using a 165 µg SO_2/m^3 static standard. These solutions were then subjected to a temperature of 50°C.

Two concentrations of $[Hg^{++}]$ were used, 0.04 M (nominal) and a 0.1 M. Table 3 indicates the results of preliminary experiments for wavelength maximum and time of full color development. The results of the stability experiments are shown in Figures 4 and 5. A summary of these stability experiments is shown in Table 4. Both the 0.04 M and the 0.1 M $[Hg^{++}]$ concentration experiments indicate that as the $[Cl^-]$ concentration increases in the ratio of $[Hg^{++}]/[Cl^-]$ from 1/2 to 1/32, the rate of decay of the sample concentration decreases to a minimum of about 19 percent and 14 percent per day, respectively.

The 0.04 M $[Hg^{++}]$ concentration reaches an optimum absorbance around 1/3 to 1/4, which is the nominal; from there on the y-intercept decreases, indicating a loss in sensitivity. Also the 0.1 M $[Hg^{++}]$ solutions give a higher sensitivity for each ratio, indicating a suppressing of color by the more $[Hg^{++}]$ concentrated solution. Based on these experiments the most stable complex is formed when the ratio of $[Hg^{++}]/[Cl^-]$ concentration is 1/16 at a $[Hg^{++}]$ concentration of 0.04 M. Although the 0.1 M $[Hg^{++}]$ 1/8 and 1/16 solutions gave slightly better stability to temperature, the amount of $[Hg^{++}]$ present and hence the amount to be disposed of was thought to be detrimental.

TABLE 3. EFFECT OF VARYING THE RATIO OF $[Hg^{++}]/[Cl^{-}]$ ON WAVELENGTH MAXIMUM AND TIME OF FULL COLOR DEVELOPMENT

$\frac{[Hg^{++}]}{[Cl^{-}]}$	MAX	TIME OF MAX COLOR
0.04 M $[Hg^{++}]$		
1/2	548 nm	30 - 60 Min.
1/3	548 nm	15 - 60 Min.
1/4	548 nm	15 - 60 Min.
1/8	550 nm	15 - 60 Min.
1/16	556 nm	15 - 60 Min.
1/32	556 nm	15 - 30 Min.
0.1 M $[Hg^{++}]$		
1/4	548 nm	15 - 60 Min.
1/8	555 nm	15 - 45 Min.
1/16	555 nm	15 - 45 Min.
1/32	570 nm	15 - 45 Min.

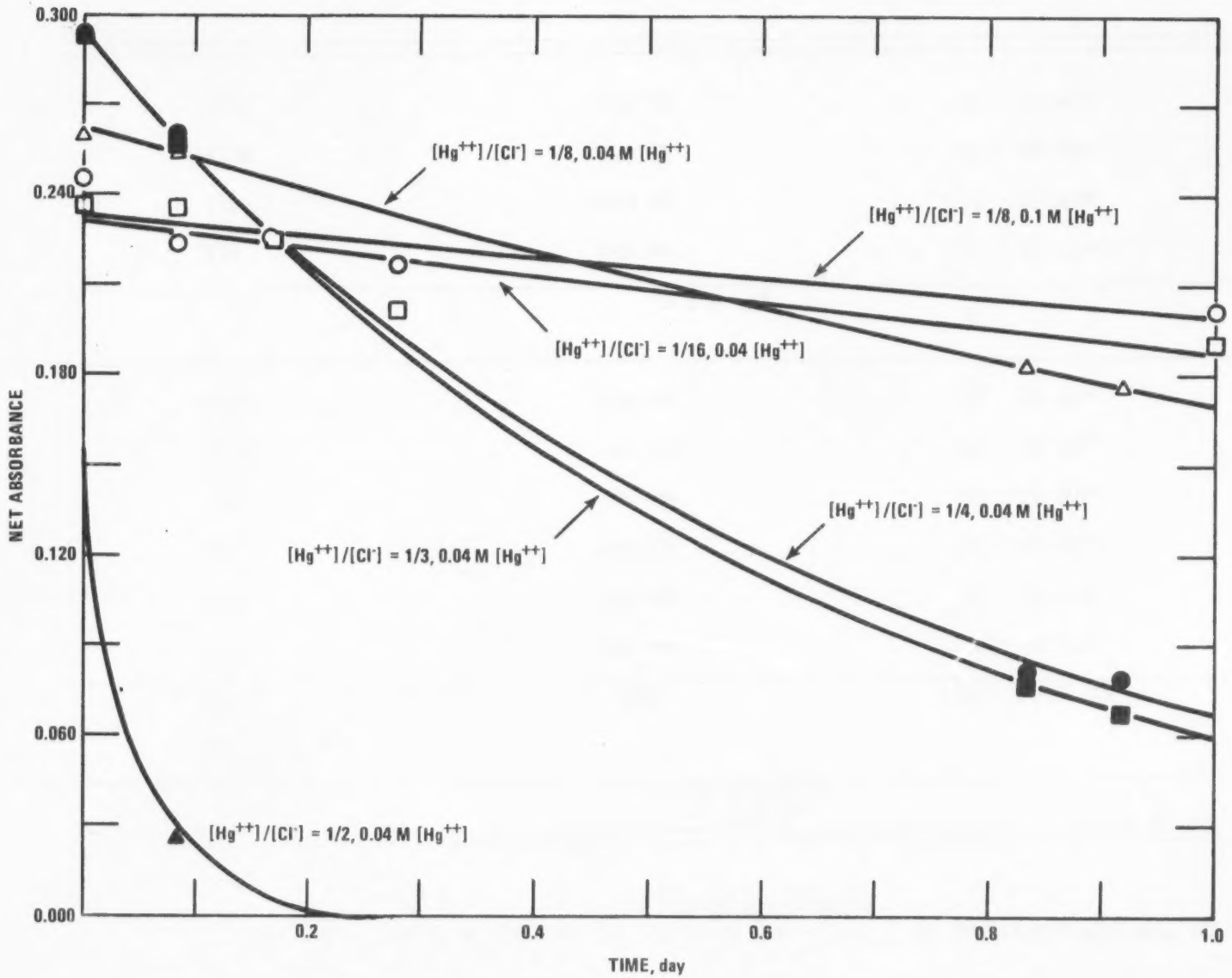

Figure 4. Effect of varying the ratio of $[Hg^{++}]/[Cl^-]$ on the stability of the dichlorosulfitomercurate complex; 50°C.

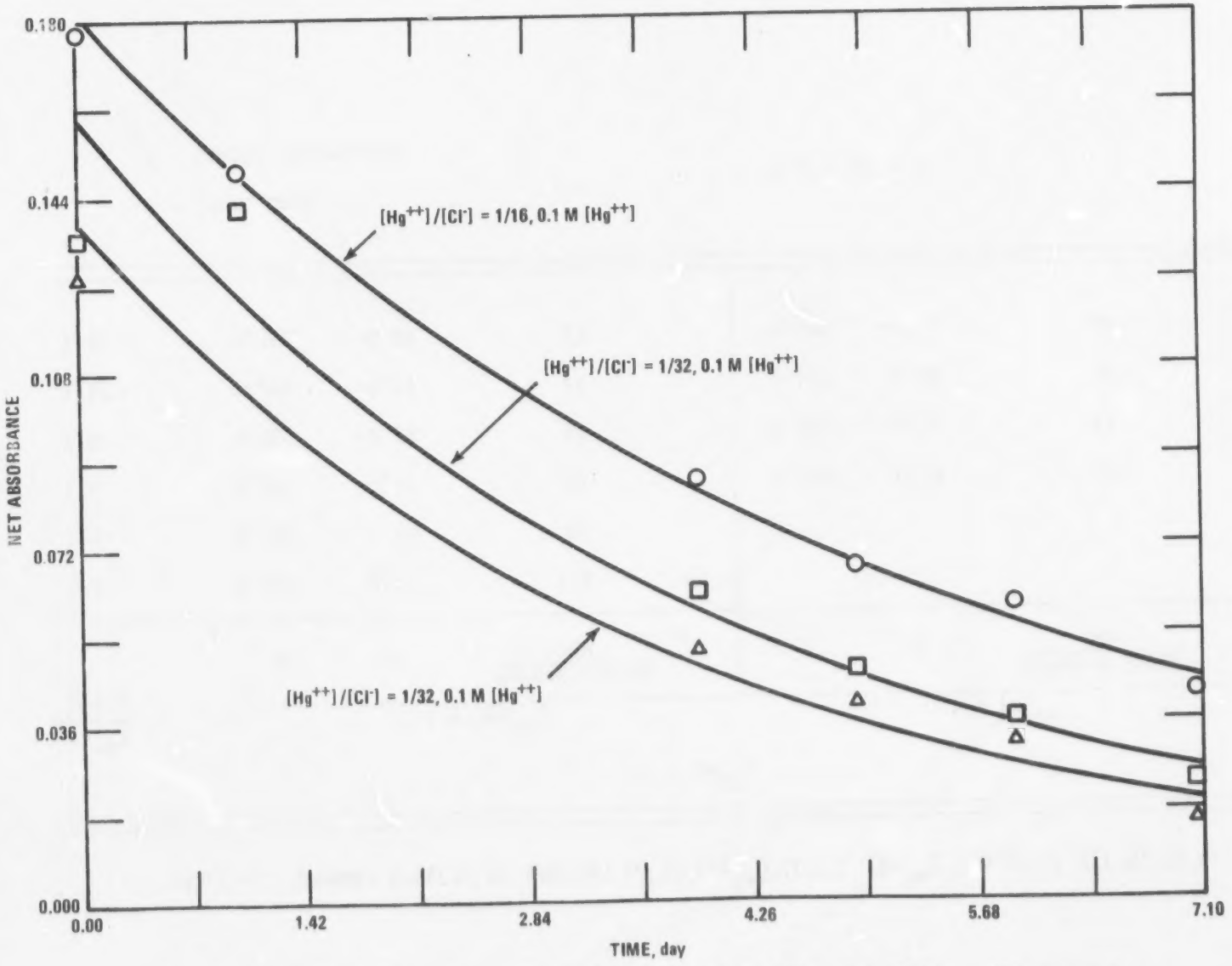

Figure 5. Effect of varying the ratio of $[Hg^{++}]/[Cl^-]$ on the stability of the dichlorosulfitomercurate complex; 50°C.

TABLE 4. SUMMARY EFFECTS OF VARYING RATIO $[Hg^{++}]/[Cl^-]$, $[Hg^{++}]$ = 0.04 or 0.1 M, 50°C

($Y = Ae^{BX}$)

$\frac{[Hg^{++}]}{[Cl^-]}$	0.4 M $[Hg^{++}]$			0.1 M $[Hg^{++}]$		
	A	B	Percent Decay / Day	A	B	Percent Decay / Day
1/2	0.267	FAST	100			
1/3	0.295	-1.60	80			
1/4	0.291	-1.47	77	0.283	-0.79	55*
1/8	0.263	-0.43	35	0.233	-0.15	14
1/16	0.231	-0.21	19	0.181	-0.20	18
1/32	0.160	-0.26	23	0.139	-0.27	24

X = Time, Days

Y = Sample Absorbance

* at a pH = 3

COLLECTION EFFICIENCY

Before going into a more detailed temperature study, the ability of this modified solution (0.04 M TCM, $[Hg^{++}]/[Cl^{-}]$ = 1/16) to collect SO_2 had to be determined. Two different SRM permeation tubes were used at different times to generate test atmospheres and were sampled with five bubbler trains in parallel for 24 hours at approximately 0.23 l/min. Initial sampling (Room Temperature) indicated plugging of the glass bubbler (narrow drawn tip with orifice of approximately 0.37 mm) during the 24 hour period in three out of five trains. The plugging was caused by a buildup of salts on the inside of the orifice tip. This experiment was repeated with the same results. The glass bubblers were then removed and replaced with identical lengths of 6 mm i.d. Teflon® tubing. No more plugging was experienced throughout the course of the experiments. The size of the orifice tip must be optimized in a typical sampling system before general use is made using the modified reagents.

Because the original experiments indicated a decrease in sensitivity, the sample aliquot was changed to 15 ml. No reagent concentration in the analysis part of the FRM was changed. The results of these experiments are listed in Table 5. The overall collection efficiency was observed to be 88.5 $\pm$ 3.4 percent. This shows a decrease in collection efficiency of about 11 percent from the 100 percent efficiency reported when using the FRM. This collection efficiency might be optimized using various size orifices to create more surface area on each air bubble.

EFFECT OF TEMPERATURE ON THE MODIFIED REAGENT

Five different sets of solution samples were prepared from $Na_2S_2O_5$ in the modified absorbing reagent to simulate ambient concentrations of 0, 49, 82, 163, and 359 µg SO_2/m^3. Each set of solutions was exposed to temperatures of 20°, 30°, 40°, or 50°C on a continuous basis. From previous experiments it was

®trade name

TABLE 5. COLLECTION EFFICIENCY OF THE MODIFIED REAGENT, 0.04 M $[Hg^{++}]$, $[Hg^{++}]/[Cl^{-}] = 1/16$

TUBE NO. 1		TUBE NO. 2	
$\frac{\mu g\ SO_2}{m^3}$	Percent Recovered	$\frac{\mu g\ SO_2}{m^3}$	Percent Recovered
36.8	93.0 ± 3.8*	39.2	90.5 ± 2.8*
36.9	86.4 ± 6.8*	84.3	86.8 ± 1.4*
167.0	86.5 ± 3.5*	178.0	85.2 ± 3.0*
417.0	90.6 ± 4.0*	410.0	88.8 ± 1.7*
	$\bar{x}$ = 89.1 ± 4.5		$\bar{x}$ = 87.8 ± 2.2
	OVERALL		
	$\bar{x}$ = 88.5 ± 3.4		

*Standard Deviation of 5 Different Sample Results.

determined that when samples, using modified reagent, were kept at 5°C for up to 36 days no decay was detected. A set of these samples plus one standard at 124 µg SO_2/m^3 was used as a standard curve; each time a set of samples was analyzed a standard curve generated from a set stored at 5°C was used as a reference.

Portions of the thermostated samples were taken and rapidly cooled to 22°C. A 15 ml aliquot was analyzed according to the analytical procedure specified in the SO_2 FRM, and the results plotted using a best fit regression curve (Figures 6, 7 and 8). No plot was made of the samples exposed to 20°C, because no decay was detected for up to 24 days. Of special note is that no concentration effect was found on the rates of decay. Table 6 summarizes the findings and compares them with our previous finding using the absorbing reagent specified in the SO_2 FRM(9). As can be seen from the summary, the rate of sample concentration decay has been drastically reduced. The modified collecting reagent has been found to increase the stability of the collected SO_2 samples over a wider temperature range. Thus the effect of temperature was reduced by about 10°C when compared against previous SO_2 FRM data.

ORDER OF REACTION

Because our data had a best fit exponential regression equation, first-order or a quasi-first order reaction is suspected. An independent check using the Van't Hoff equation verified this.

$$\ln V = \ln k + n \ln c$$

where v = velocity of reaction, total µg SO_2/day

k = rate of decay, day^{-1}

n = order of reaction, slope of line

c = concentration of sample, total µg SO_2.

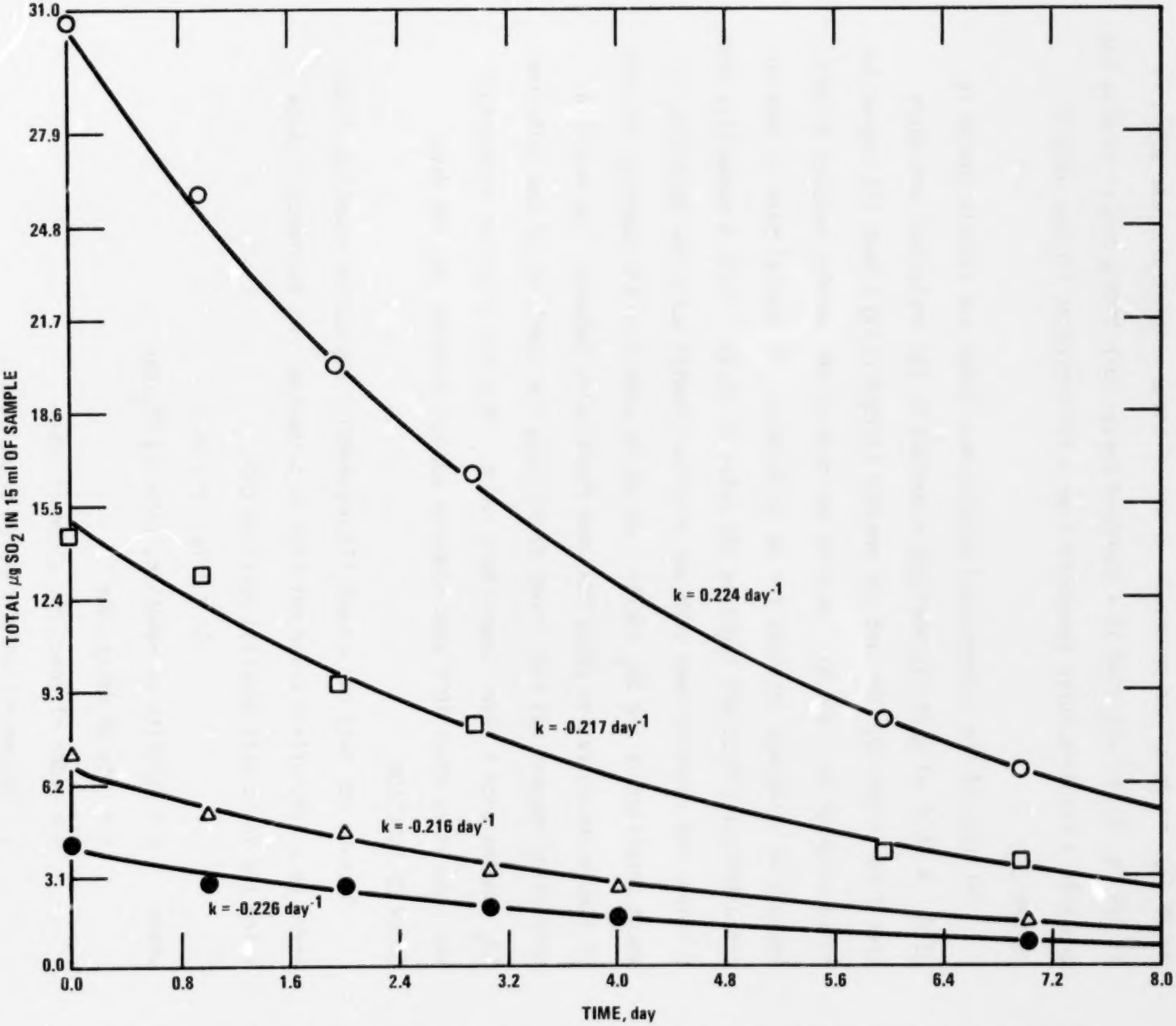

Figure 6. Effect of temperature on stability of the modified dichlorosulfitomercurate complex, 50°C.

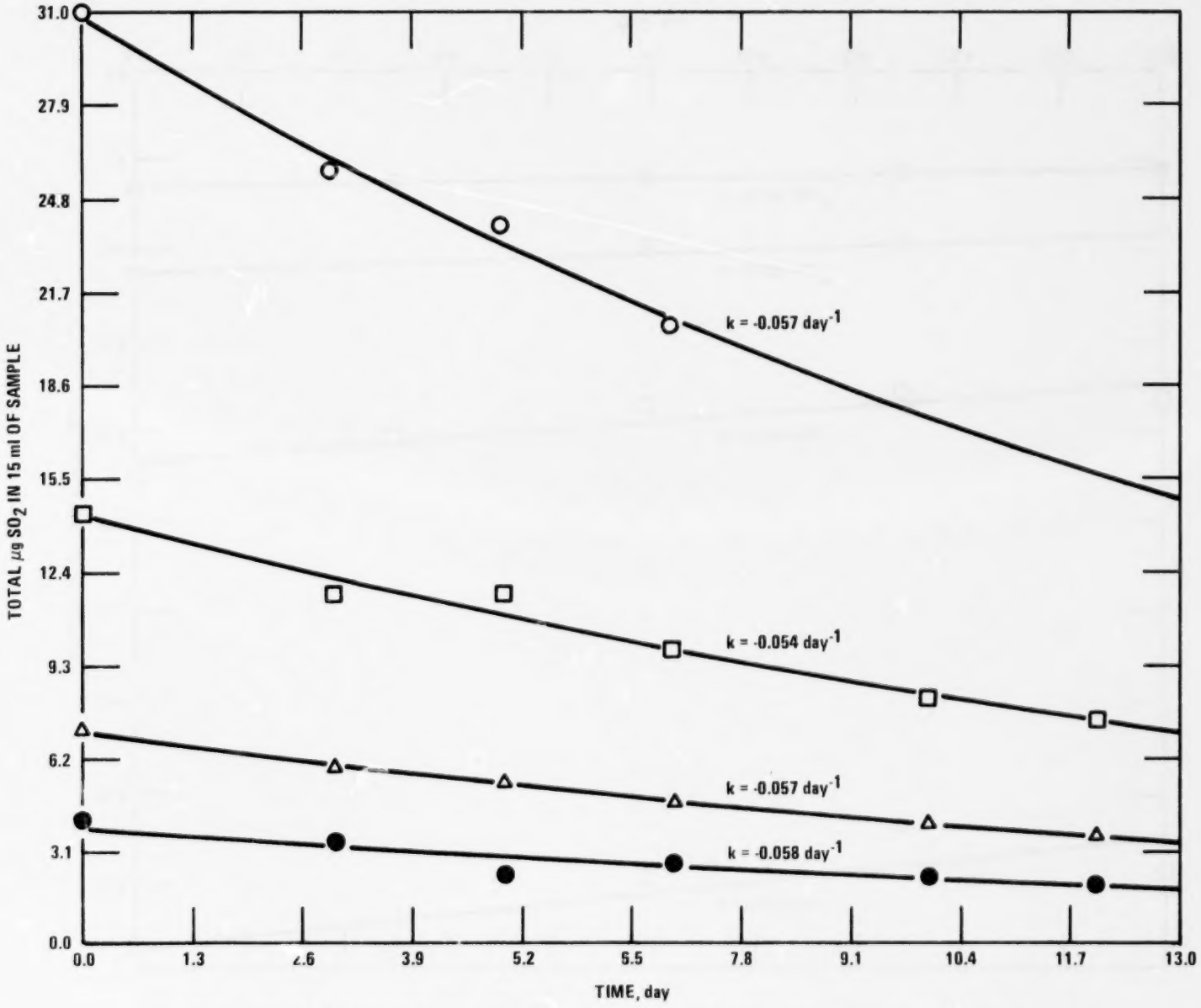

Figure 7. Effect of temperature on stability of the modified dichlorosulfitomercurate complex, 40°C.

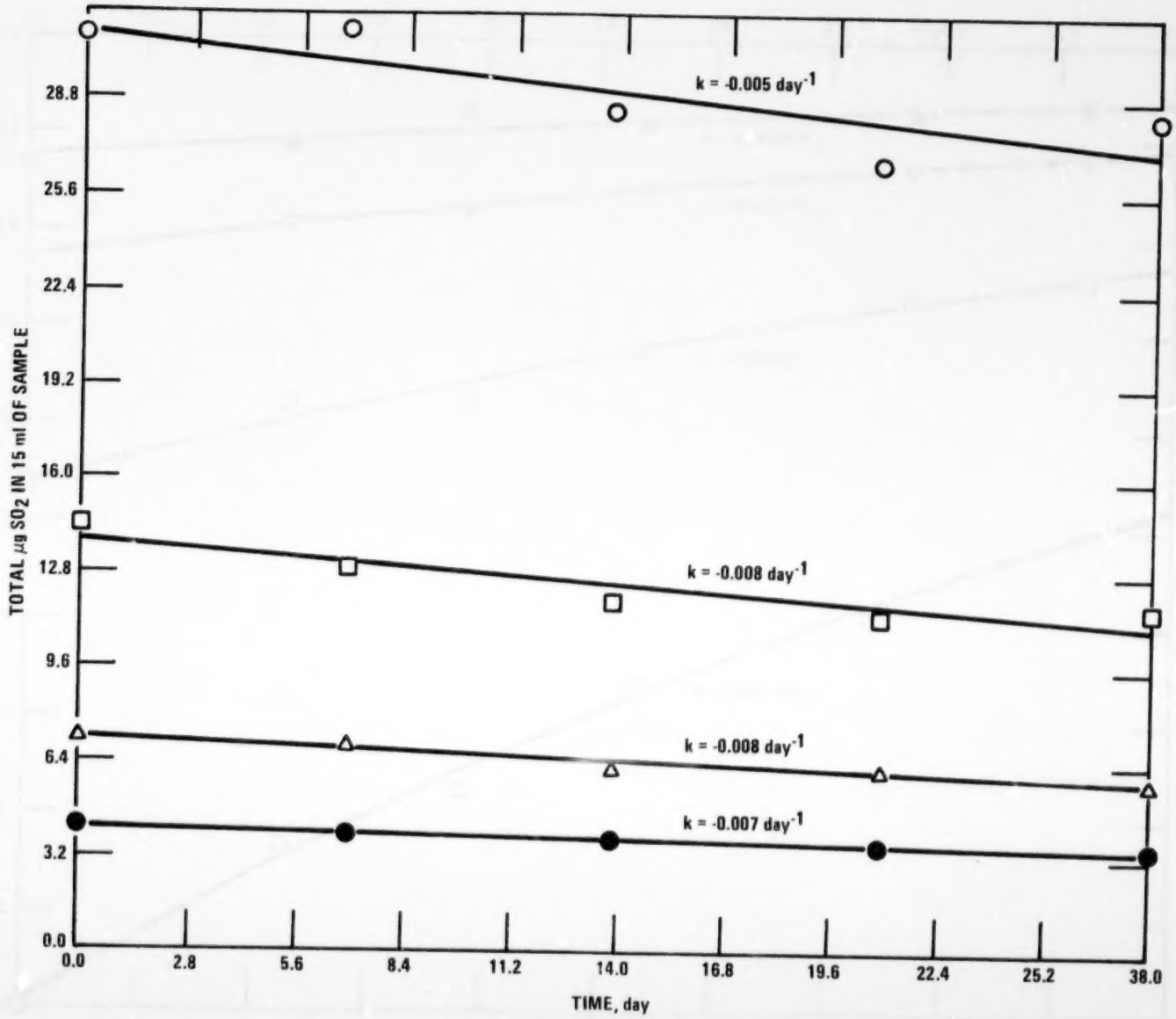

Figure 8. Effect of temperature on stability of the modified dichlorosulfitomercurate complex, 30°C.

TABLE 6. COMPARISON OF THE TEMPERATURE STABILITY OF THE DICHLORCSULFITOMERCURATE COMPLEX

	PERCENT DECAY/DAY	
TEMP.	FRM TCM	MODIFIED TCM
50°C	74.	20.
40°C	25.	5.5
30°C	5.0	0.8
20°C	0.9	*

*No loss detected after 24 days

These plots must give a straight line for this equation to estimate order of reaction (Table 7).

ANNHENIUS EQUATION

To expand the usefulness of the temperature decay rate data use is made of an Arrhenius plot. When the logarithm of the decay rate (k) is plotted against the inverse of the absolute temperature, a linear relationship results if the activation energy remains independent of the temperature.

$$k = Ae^{(-E/RT)}$$

where k = rate of reaction (decay), day^{-1}

A = frequency factor, day^{-1}

E = energy of activation, calories/mole

R = gas constant, 1.987 calories/degree-mole

T = absolute temperature of reaction, K

Figure 9 is an Arrhenius plot of our data

where $\ln k = \ln A - (\frac{E}{R})\frac{1}{T}$

$$\ln k = 49.284 - 16385\ (\frac{1}{T}).$$

The point k = 0.005, 30°C was deleted from the derivation of the equation because of its own variable plot (Figure 8). To adequately describe the effect at 30°C, a much longer time to allow measurable sample concentration decay is necessary to overcome small variations in sample absorbance readings.

From this equation rates of decay within the measured range and slightly to the outside can be calculated with confidence. This equation also indicates that the activation energy is equal to 32.6 kcal/mole. The activation energy of the SO_2 FRM reaction was calculated to be 31.2 kcal/mole(9). Increasing the $[Cl^-]$ concentration in the $[Hg^{++}]/[Cl^-]$ ratio from 1/4 to 1/16 increases the energy of activation 1.4 kcal/mole.

TABLE 7. DETERMINATION OF ORDER AND REACTION RATE

Temp °C	Order of Reaction	ln k	Estimate of k
50	0.9987	-1.508	-0.221
40	0.9860	-2.844	-0.058
30	1.103	-5.082	-0.006

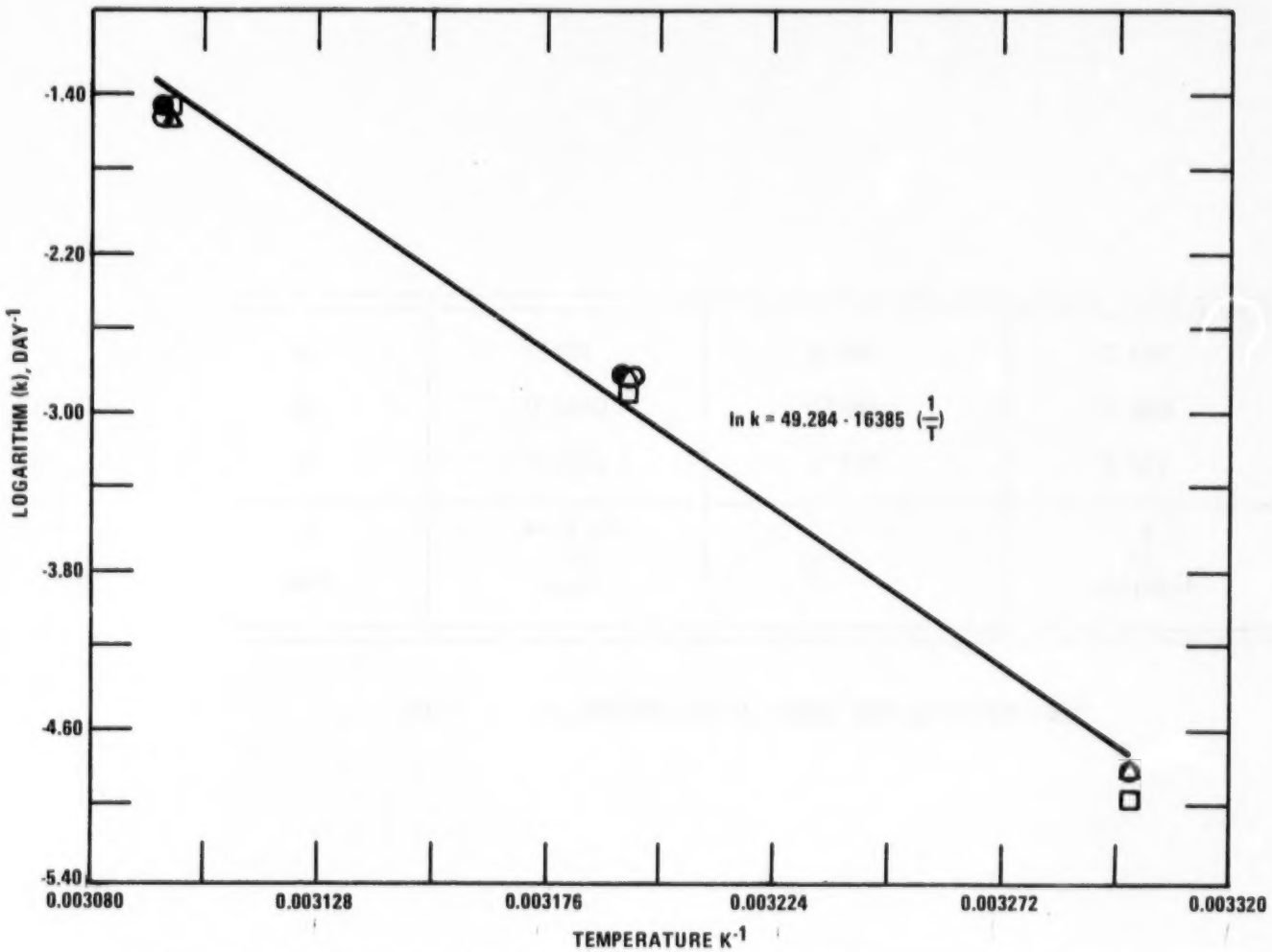

Figure 9. Effect of temperature on decay rate constant of dichlorosulfitomercurate complex.

COMPARING THE EFFECT OF VARYING TEMPERATURE ON THE SO_2 FRM AND OUR MODIFICATION

Using the mathematical model, we derived in a previous project (9), a theoretical comparison of temperature effect on an ambient collected sample experiencing a typical spring and summer day here at the Research Triangle Park, N.C., was derived and shown in Table 8. This table quite dramatically shows the decrease in decay that would be experienced if the suggested modification were incorporated. However, these temperatures reflect the ambient temperature, not the temperature inside a bubbler box sampler.

GENERAL INFORMATION

(a) During the major temperature study, standard samples stored at 5°C were analyzed with the following results over a period of a month.

$n = 12$ $\quad\quad$ $\bar{R}^2 = 0.9992$

average slope 0.0218

standard deviation $\pm$ 0.0008

average blank measured 0.094 absorbance units

average y-intercept 0.089 absorbance units

A difference of measured blank and y-intercept of greater than 0.015 absorbance units indicated a significant difference between the two and they could not be considered equal.

(b) As a check on the ability of the spectrophotometer to make a consistent measurement, a Standard Reference Material 930c purchased from the National Bureau of Standards consisting of one blank and three neutral density filters were measured for absorbance over the periods of analysis. Although the filters were calibrated by NBS at other wavelengths they were measured at the wavelength of maximum absorbance (556 nm) as

TABLE 8. EFFECTS OF TEMPERATURE EXPERIENCED ON SPRING AND SUMMER DAYS ON THE OVERALL DECAY RATE OF THE FRM AND THE MODIFIED REAGENT

SPRING DAY	SUMMER DAY
16 Hours 22°C (72°F)	16 Hours 22°C (72°F)
4 Hours 25°C (77°F)	4 Hours 30°C (86°F)
4 Hours 30°C (86°F)	4 Hours 35°C (95°F)
FRM 2.2 Percent Decay / Day	FRM 3.8 Percent Decay / Day
MODIFIED 0.3 Percent Decay / Day	MODIFIED 0.6 Percent Decay / Day

a quality assurance check. The three gave average (n = 16) values of 0.510 ± 0.001, 0.722 ± 0.001, and 1.016 ± 0.001, indicating proper operation of the spectrophotometer during analysis.

(c) During the project it was noted that when the nominal formaldehyde (HCHO) concentration (0.2 percent) was increased, the developed absorbance decreased, and as the nominal HCHO concentration decreased, there was a slight increase in absorbance.

HCHO CONCENTRATION
(Nominal = N)

	(1/3)N	(1/2)N	(1)N	(2x)N	(3x)N
PERCENT MEASURED	108	107	100	83	74

The increase in HCHO concentration decreased the sample absorbance and increased the absorbance of the blank; the reverse was also true.

BLANK ABSORBANCE
(Nominal = N)

	(1/3)N	(1/2)N	(1)N	(2x)N	(3x)N
PERCENT MEASURED	83	92	100	132	170

The age of the HCHO solution (0.2 percent) is also critical and should be optimized if this modification is used. Preliminary experiments indicate that the HCHO solution should be prepared immediately prior to addition. As the age of the HCHO solution increased, the sensitivity of the measurement decreased. Accuracy is not affected because all measurements would be relative to a daily static calibration.

SECTION 4

CONCLUSIONS

This project was undertaken for the purpose of determining if any change in reagent concentration or condition in the SO_2 FRM could bring about substantial retardation of the effect of temperature on the stability of the formed complex. By increasing the amount of the chloride ion ($[Hg^{++}]$ = 0.04 M), we have essentially reduced the decay rate of the formed TCM-SO_2 complex by an effect of 10°C. The improvement we have developed here could be used to liberalize the sample temperature specification required to protect the integrity of the collected SO_2 sample.

However, this modification does not erase all temperature specifications for sample handling and if this modification is to be used routinely further optimization of some physical parameters (i.e., bubbler tip size) must be accomplished.

SECTION 5

RECOMMENDATIONS

Based on the temperature sensitivity of the SO_2 FRM both during sampling and prior to analysis, certain temperature specifications(16) were recommended to all Environmental Protection Agency Regions in their handling of the 24 hour SO_2 sample when using the Pararosaniline Method. It was suggested that sampling be carried out in such a manner that the TCM absorbing reagent be maintained at 25°C or less during sampling and that the collected samples be maintained at 20°C or less until analysis.

What this effectively suggests is that during sampling and prior to analysis the sample decay should not exceed one percent per day. Even though the sample decay rate at 25°C is 2.4 percent per day (FRM), the whole amount is not present at the beginning and the decay can best be estimated during sampling to be one half of the decay of a collected sample that sat at 25°C for 24 hours.

As indicated in this report, increasing the $[Cl^-]$ concentration in the ratio of $[Hg^{++}]$ to $[Cl^-]$ from 1/4 to 1/16 (0.04M Hg^{++}) effectively reduces the temperature sensitivity of the formed complex by 10°C. Therefore, maintaining the same decay rate specification as originally suggested would mean a sampling temperature of 35°C or less and a shipping and storage temperature of the collected sample not to exceed 30°C. Although this drastically reduces the temperature control needed on sampling and storage of the sample, it does not erase it completely; some temperature control is still necessary.

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